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(54) **Endosseous implants.**

(57) Endosseous implants are produced by thermally spraying a ceramic material onto the surface of a metallic core material having rough surface, i.e. a maximum surface roughness of 15 to 100 um. The implants have the characteristics of both the metallic material and ceramic material and do not dissolve out harmful metal ions. The endosseous implants are useful for implantation in various bones including tooth roots and joints in living bodies.

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ENDOSSEOUS IMPLANTS

This invention relates to endosseous implants and to a method for producing them.

Implantation technology, which comprises the insertion of artificial materials such as artificial organs, artificial blood vessels, artificial joints, artificial bones and artificial tooth roots into the body, has attracted much attention in recent years. It is said that trials of implantation go back to ancient times. Particularly in the last ten years, a huge number of treatments by implantation have been performed on bones and tooth roots to afford good results in the remedy of defects or the recovery of functions thereof. However, there has not yet been obtained an artificial bone or tooth root which satisfies the necessary requirements as a material for living bodies, i.e. affinity to living tissue, safety and excellent durability.

As metallic materials which have mainly been used for preparation of artificial bones or tooth roots, cobalt-chromium alloys, stainless steel, titanium and tantalum are exemplified. On the other hand, as ceramic materials, alumina or materials comprising predominantly carbon have been recently taken note of.

Although metallic materials are excellent in mechanical strength, particularly in impact strength, they lack affinity for living tissue. For example, when a metallic implant is used, metal ions are dissolved out therefrom and are toxic to bone cells around the implant. Furthermore, bone-formation is obstructed, probably because of too large a thermal conductivity of the metallic implant. Among the metallic materials, titanium and tantalum are particularly superior in a corrosion-resistance and hence have been employed as fixing plates for skulls

or fractured parts of bones and implants of jawbones since about 1940, but these are not necessarily satisfactory.

On the other hand, ceramic materials generally show a good affinity to bones, and tissues penetrate into fine pores of ceramic materials to afford a strong fixation, without adverse reaction between the ceramic material and the tissue. Besides, they are also excellent in durability, that is, they are resistant to corrosion or decomposition. On the other hand, they possess a poor impact strength.

There has been proposed an implant having the characteristics of both metallic materials and ceramic materials, i.e. an implant prepared by thermally spraying a ceramic material onto the surface of a metallic core material (cf. Japanese Patent First Publication Nos. 14095/1977, 82893/1977, 28997/1978 and 75209/1978). In these methods, however, a self-bonding type bonding agent is used in order to improve the adhesion of the ceramic coating layer. The bonding agent has the problem that it contains nickel, chromium, etc. which dissolve out in living tissue and have toxic effects on the body.

The present invention provides endosseous implants prepared by thermally spraying a ceramic material onto a metallic core material having a rough surface. More particularly, there is provided a method for producing an endosseous implant by thermally spraying a ceramic material onto a metallic core material having a maximum surface roughness of 15 to 100 μm.

In one embodiment, titanium hydride is thermally sprayed onto the surface of a metallic core material for making rough the surface thereof to a maximum surface roughness of 15 to 100 μm, and then a ceramic material is thermally sprayed thereon. In

another embodiment the metallic core material is roughened by etching with an acid to a maximum surface roughnesss of 15 to 100 μm, and then a ceramic material is thermally sprayed thereon.

The present invention will now be further described by way of example only with reference to the accompanying drawings, in which:

Figure 1 is a schematic view of an embodiment of the endosseous implant for the lower jawbone of a dog, wherein 1 represents the lower jawbone, 2 and 3 are natural teeth, 4 is an artificial tooth root and 5 is an artificial tooth crown attached on the artificial tooth root 4.

Figure 2 is a schematic view of an embodiment of the endosseous implant of blade type for the jawbone according to this invention, and (A) is a front view thereof and (B) is a side view thereof, wherein 6 represents a metallic implant (core material) and 7 is a ceramic layer containing unopened pores which do not reach the metal surface.

According to the present invention, as is shown in Figure 2, a ceramic coating is applied to the surface of a metallic implant core material so as to obtain an implant with good impact strength and interacting with the surrounding bone tissues in a similar manner to ceramic materials.

The metallic core materials used in this invention may be any suitable materials which have appropriate mechanical strength and are not harmful to the body, including those materials which have usually been used as artificial materials for bones, joints and tooth roots which do not exhibit harmful effects on living tissue and possess an appropriate mechanical strength, for example, cobalt-chromium alloys, stainless steels, titanium, titanium alloys, tantalum or zirconium. Among these materials,

preferred are titanium, titanium alloys, zirconium and tantalum in view of their excellent corrosion resistance. Most preferred are titanium and titanium alloys (e.g. 6 % Al-4 % V-Ti, etc.) in view of their excellent processability and safety.

The ceramic materials used in this invention may be, for example, hydroxyapatite, calcium phosphate, aluminum oxide, zirconium oxide or titanium oxide, which may be used alone or in combination of two or more thereof. In order to control the pores in the ceramic layer, porcelain may be applied by thermally spraying it together with the ceramic material or by baking it on the ceramic coating layer. For such a purpose, there can be used porcelains such as Dentin and Enamel, for example. Among the ceramic materials, preferred are hydroxyapatite and aluminum oxide in view of their excellent affinity with living tissue. A combination of hydroxyapatite and aluminum oxide is particularly suitable because it interacts most intimately with living tissue.

The endosseous implants of this invention can be produced in the following manner.

The metallic material is formed into the desired shape, for example by conventional methods, such as cutting, casting, forging, punching, electro-arc machining, laser-processing, or powdered metal technique. The surface of the metallic core material thus formed is roughened to a specific maximum surface roughness. The maximum surface roughness of the metallic core materials is in the range of 15 μm to 100 μm, the inventors having measured the roughness by the method described in JIS B-0601. When the maximum surface roughness is smaller than 15 μm, the thermally sprayed ceramic coating layer shows insufficient adhesion. On the other hand, when it is

larger than 100 μm, it is disadvantageously difficult to form a thin uniform layer of the ceramic coating. The most suitable maximum surface roughness is in the range of 20 to 60 μm in view of the adhesion and uniformity of the coating layer.

In order to roughen the surface of the metallic core materials, various methods may be applied, for example, mechanical methods such as grinding, sandblasting, grit blasting, etc.; chemical etching, e.g. treatment with an acid or alkali; electrolytic etching; and forming a titanium layer with a rough surface by thermally spraying titanium hydride powder. Among these methods, preferred are blasting, chemical etching, and forming a titanium layer with a rough surface, because the ceramic material can easily bite into the rough surface.

The chemical etching is usuually carried out by using mineral acids, for example sulfuric acid, hydrochloric acid or hydrofluoric acid, which may be used alone or in a combination of two or more thereof. When blasting is combined with etching with an acid, particularly when the metallic core material is firstly subjected to blasting and then to etching with an acid, the core material shows extremely preferable adhesion of the coating layer. Besides, when the metallic core materials are coated with titanium having a rough surface by thermally spraying titanium hydride powder, it is preferable to previously subject the materials to the above surface-roughening treatments, for example mechanical treatment (e.g. grinding, sandblasting, grit blasting), chemical etching with an acid or alkali or electrolytic etching. The thermal spraying of titanium hydride is preferably carried out by thermal plasma spraying. The particle size of the titanium hydride is not particularly limited, but is

preferably in the range of 10 to 100 μm. The titanium coating layer substantially does not release any harmful metal ion, unlike the self-bonding type bonding agent-containing metals which are easily dissolved out in living tissue.

In the thermal spraying of ceramic materials, any portion which is not coated with the ceramic material is previously masked by an appropriate means, for instance, application of a marking ink or an aluminum adhesive tape prior to the treatment for roughening the surface. The thermal spraying of the ceramic material is also preferably carried out by a thermal plasma spraying apparatus. Some portions of the endosseous implants, for instance, the ceramic coating layer in artificial joints, are required to be highly smooth. In such a case, a porcelain is coated onto the surface and the coated product is repeatedly calcined in a vacuum furnace.

In the endosseous implants of this invention, the thickness of the ceramic coating layer which optionally contains porcelain is not particularly limited, but is preferably in the range of 10 to 200 μm.

This invention is illustrated by the following Examples but should not be construed to be limited thereto. In the Examples, the surface roughness figures are as measured by the method of JIS B-0601.

Example 1

A core material for an endosseous implant is prepared from a titanium material (JIS, second class of material) by cutting and grinding the titanium material by electro arc machining.

The metallic core material for the implant is grit-blasted with a blast apparatus [a mammoth type ventiblast apparatus, manufactured by Metco Inc., England; blasting agent: Metcolite VF, manufactured

by Metco Inc.; pressure: 30 psi (205 kPa)]. The thus-blasted material has a maximum surface roughness of 10 μm.

The blasted core material is dipped in 30 % sulfuric acid solution at 50°C for 72 hours to effect etching. After the etching, the core material has a maximum surface roughness of 50 μm.

Under an argon-hydrogen-plasma jet flame (ARC electric current 500 Amp) generated by a plasma spray apparatus (6MM-630 type, manufactured by Metco Inc., equipped with an electric power supplier), a ground mixture of hydroxyapatite (particle size: 10 - 100 μm, 80 % by weight) and aluminum oxide (WA #120, manufactured by Nippon Kenmazai K.K., 20 % by weight) is thermally sprayed to form a coating layer having a thickness of about 150 μm on average. The thermally sprayed coating layer has excellent adhesion, and even when the product is subjected to bending processing at an angle of 160°, the coating layer is not peeled off.

The product obtained above was tested as follows:

The implant was embedded into the lower jawbone of a dog. After 3 months, it was observed by X-ray fluoroscopy. As a result, formation of dense bone around the implant was confirmed.

Example 2

A core material for an endosseous implant is prepared from a titanium material (JIS, second class of material) by cutting and grinding the titanium material by electro arc machining.

The metallic core material for the implant is grit-blasted with a blast apparatus [a mammoth type ventiblast apparatus, manufactured by Metco Inc., England; blasting agent: Metcolite VF, manufactured by Metco Inc.; pressure: 30 psi (205 kPa)]. The

thus-blasted material has a maximum surface roughness of 10 μm.

Under an argon-hydrogen-plasma jet flame (ARC electric current 500 Amp) generated by a plasma spray apparatus (6MM-630 type, manufactured by Metco Inc., equipped with an electric power supplier), titanium hydride powder (Powder No. XP-1157, manufactured by Metco Inc.) is thermally sprayed, as the first coating layer, onto the blasted core material to form a first coating layer of about 50 μm in thickness over the whole surface thereof. As the second coating layer, a mixture of hydroxyapatite (particle size 10 - 100 μm, 80 % by weight) and aluminum oxide (WA #120, manufactured by Nippon Kenmazai K.K. 20 % by weight) is thermally sprayed to form a coating layer having a thickness of about 150 μm on average. The thermally sprayed coating layer has excellent adhesion, and even when the product is subjected to a bending process at an angle of 160^{o}, the coating layer is not peeled off.

The product obtained above was tested as follows:

The implant was embedded into the lower jawbone of a dog. After 3 months, it was observed by X-ray fluoroscopy. As a result, there was confirmed formation of dense bone around the implant.

<u>Reference Example</u>

A core material for an endosseous implant is prepared by treating the same titanium material in the same manner as described in Example 1. The core material is likewise subjected to grit blasting, but is not subjected to etching. The material has a maximum surface roughness of 10 μm which is about 1/5 of that of the core material before thermal spraying in Example 1.

The blasted core material is thermally sprayed

with a mixture of hydroxyapatite and aluminum oxide in the same manner as in Example 1 to give a coating layer having a thickness of about 150 µm on average. The resulting product has significantly inferior adhesion of the coating layer and the coating layer is easily peeled off even by a light impact. Thus, this product cannot be used as an endosseous implant.

It will be appreciated from the foregoing that in accordance with the invention there may be provided endosseous implants comprising a metallic core whose surface is roughened to a maximum roughness of 15 to 100 µm and a ceramic material directly bonded to the metallic core without a bonding agent. Preferably, roughening is provided by a titanium layer on the metallic core and, optionally, the surface of the metallic core below the titanium layer is roughened. This roughening of the surface of the metallic core which acts as a substrate for the titanium layer may be achieved by blasting or chemical etching or both.

It will also be seen from the foregoing that we have provided an endosseous implant which has good impact strength and the affinity for living tissue of ceramics but need not release toxic metal ions into the body.

CLAIMS:

1. A method for producing an endosseous implant, comprising roughening the surface of a metallic core material to a maximum surface roughness of 15 to 100 μm and then thermally spraying ceramic material onto the roughened surface of the metallic core material.

2. A method according to claim 1, wherein the surface of the metallic core material is roughened by subjecting the core material to etching with an acid.

3. A method according to claim 2, wherein the surface of the metallic core material is subjected to blasting before the etching.

4. A method according to claim 1, wherein the surface of the metallic core material is roughened by thermally spraying titanium hydride onto the surface of the core material.

5. A method according to claim 4, wherein the surface of the metallic core material is subjected to blasting or etching with an acid or both before being thermally sprayed with titanium hydride.

6. A method according to any one of the preceding claims, wherein the metallic core material has a maximum surface roughness of 20 to 60 μm.

7. A method according to any one of the preceding claims, wherein the ceramic material for thermal spray coating comprises hydroxyapatite.

8. A method according to any one of claims 1 to 6, wherein the ceramic material for thermal spray coating comprises a mixture of hydroxyapatite and aluminum oxide.

9. An endosseous implant comprising a metallic core whose surface is roughened to a maximum surface roughness of 15 to 100 µm and a ceramic material thermally sprayed onto the roughened surface.

10. An endosseous implant according to claim 9, wherein the roughening of the metallic core is provided by a titanium layer thereon.

Figure 1

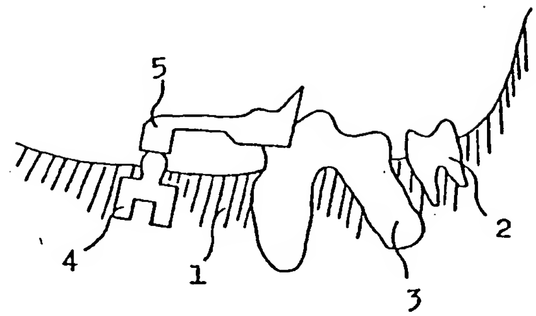

Figure 2

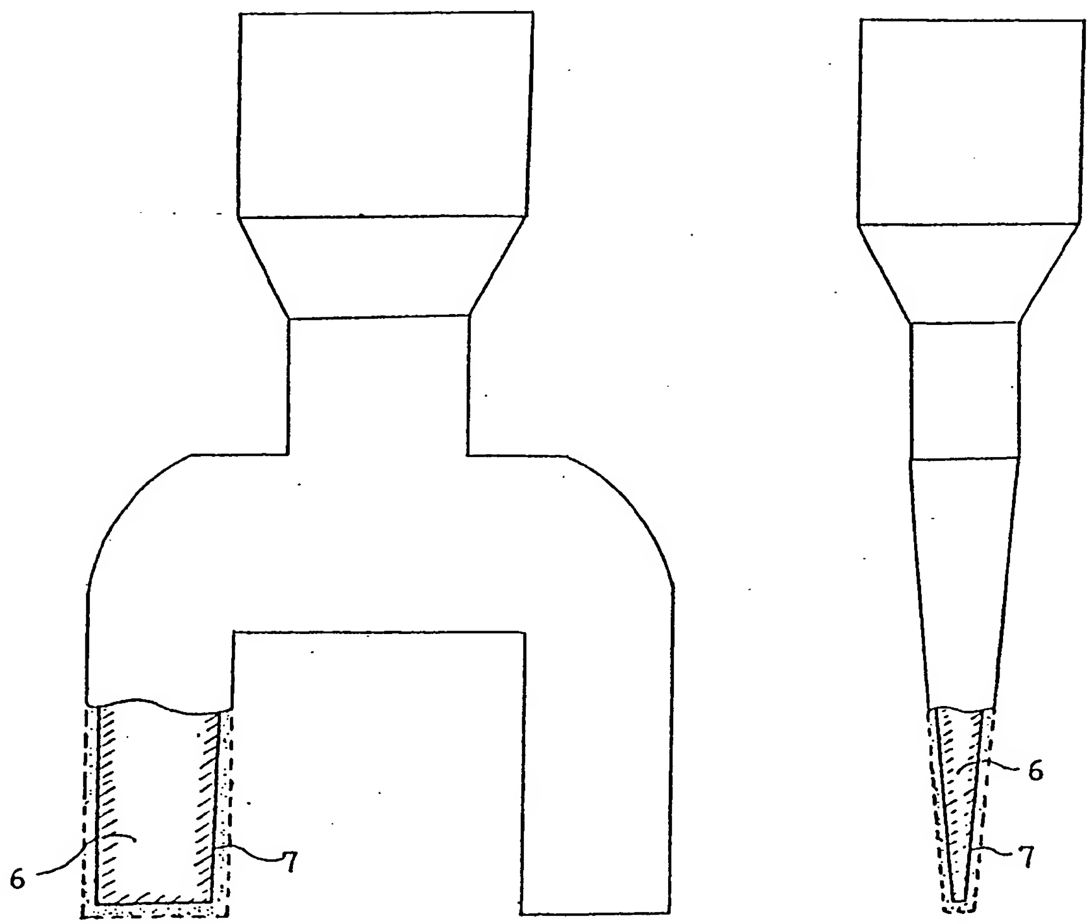

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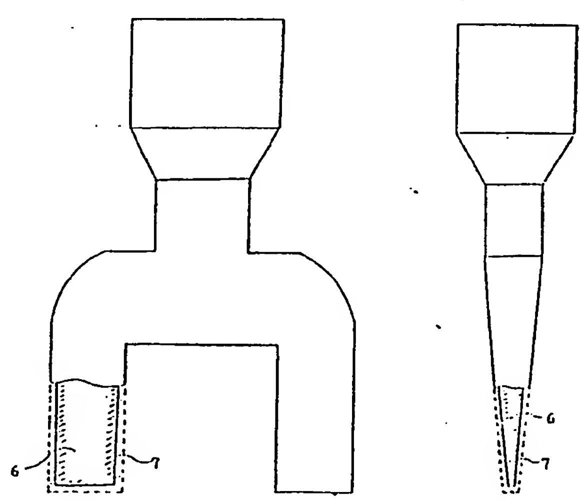
Figure 2



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EUROPEAN SEARCH REPORT

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Application Number

EP 86 30 6173

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE-A-2 313 678 (BECKER et al.) * claims 1,4,5 * ---	1,9	A 61 F 2/30 A 61 C 8/00 A 61 L 27/00
A	FR-A-2 374 020 (ONTARIO RESEARCH FOUNDATION) * claims 1,6,8,9 * ---	1,4,9	
A	FR-A-2 318 617 (SUMITOMO CHEMICAL CO., LTD.) * claims 8,9 * & JP - A - 52 014 095 (Cat. D,A) ---	1	
A	FR-A-2 336 913 (SUMITOMO CHEMICAL CO., LTD.) * claims 16,22 * & JP - A - 52 082 893; & JP - A - 53 028 997 (Cat. D,A) ---	1	
A	FR-A-2 374 019 (SUMITOMO CHEMICAL CO., LTD.) * claims 5,6 * & JP - A - 53 075 209 (Cat. D,A) -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			A 61 C 8/00 A 61 F 2/00 A 61 L 27/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	21-12-1987	KANAL P K

CATEGORY OF CITED DOCUMENTS

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